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THE MECHANISMS OF PLASTIC DEFORMATION OF POLYMERS AND THEIR RATE DEPENDENCE

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The Mechanisms of Plastic Deformation of Polymers and

Their Rate Dependence

Final Report

Arthur P. L. Turner - Principal Investigator

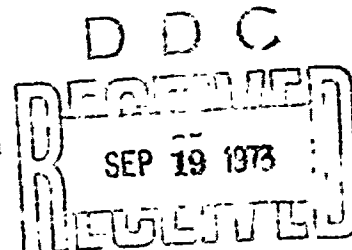July 27, 1973

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13. ABSTRACT

A research program directed toward gaining an understanding of the molecular mechanisms of large strain deformation in glassy and crystalline polymers has been carried out. The investigation encompassed two types of experimental procedures: deformation experiments on bulk polymers to determine the thermal activation parameters of the rate limiting step of the deformation process, and microscopic examination of deformed samples to determine what types of molecular motions had taken place. Macroscopic deformation experiments were performed of polycarbonate and polyethylene. Activation enthalpies, shear activation volumes, and dilatation activation volumes were determined for each polymer. Microscopic studies were performed on extended chain crystalline polyethylene which had a spherulitic structure. Deformation was found to occur on discrete shear bands. The spherulitic structure did not seem to strongly affect the deformation. Microscopic examination revealed that deformation could take place by intralamellar slip in any direction on any plane parallel to the direction of the molecules, by interlamellar shear, and by formation of kinks.

The behavior of shear bands in polycarbonate is also discussed, and a technique for producing metallic replicas of polymer surfaces is described.

14. KEY WORDS

Plastic Deformation	Crystalline Polymers	Polyethylene
Polymers	Bulk Polymers	
Glassy Polymers	Polycarbonate	

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Table of Contents

I. Introduction - Purpose of the Research Program

The purpose of this research program was to study the nature of large strain plastic deformation of polymers with the intent of gaining an understanding of the molecular level mechanism of the deformation. The ultimate goal of the project was to develop a model for the molecular motions which occur during the deformation process and to identify the critical rate limiting step in the process. The studies undertaken in this program were of two different types: 1) macroscopic deformation experiments of the thermal analysis type designed to measure the parameters of the thermally activated rate limiting step of the deformation. 2) microscopic examination of deformed polymer structures to determine what molecular motions can occur. Thermal analysis measurements were made on polycarbonate (Lexan), which is amorphous, and on high molecular weight polyethylene (Allied Chemical AC1220) which is crystalline. Microscopic studies were made of extended chain polyethylene which was prepared by crystallization under pressure to give a spherulitic structure of extended chain crystals.

II. Summary of the Research

A. Shear Bands in Polycarbonate

Bulk deformation experiments were carried out in the mode of torsion of tubular samples. This mode was chosen to suppress the instability associated with necking and drawing, which is characteristic of tensile deformation of most ductile polymers. Early in the work on deformation of polycarbonate, it was found that plastic yield in torsion was accompanied by a small drop in the stress even in the absence of a change in the cross sectional area

of the sample so that the material was undergoing a true work softening
instability. Microscopic examination of the samples revealed that the
yielding process was accompanied by the formation of fine deformation
bands similar to those observed in other glassy polymers by a number of
investigators (1,2). Most other investigations of shear bands have employed
compression specimens with stress concentrating notches to produce the
shear bands and to suppress crazing and fracture. In these experiments,
the shear bands are often growing in a stress gradient, and instabilities
associated with the deformation are a common problem. Since the experiments
in this investigation employed torsional loading, the stress was relatively
uniform throughout the sample and no serious instabilities were encountered.
The project, therefore, took advantage of the opportunity offered to exten-
sively study the process of deformation through the mechanism of shear band
formation and growth. The results of this study are described in detail
elsewhere (3), (The manuscript of this paper is submitted as Rept. No.
DAHC04-71-C-0037-1.) so only the important findings are summarized here.

Deformation of polycarbonate to a shear strain of approximately 70%
at room temperature and atmospheric pressure takes place by the process of
growth of shear bands. During this stage of deformation, the strain dist-
ribution in the samples is inhomogeneous being the full 70% inside the shear
bands and less than 10% outside the bands. The deformation outside the
bands is viscoelastic and relaxes with time after the load is removed, while
the strain inside the bands is plastic and remains in the sample indefinitely
unless the sample is annealed. Fine shear bands originate at the maximum in
the stress-strain curve. After initiation of the bands, the nominal stress
in the sample drops slowly when straining is continued at the same rate, and

the bands grow in length to encircle the sample. The drop in the nominal stress amounts to about 10%. After the bands have encircled the sample, they begin to broaden along the gage section of the sample until they cover the entire gage section and the sample contains a uniform strain of 70%. The growth in the width of the bands along the specimen axis occurs at a relatively constant stress. A typical torque twist curve for a sample is shown in Fig. 1. Pictures of the bands in various stages of development are shown in Fig. 2.

If the sample is unloaded, after the deformation bands have been formed, and twisted in the opposite direction, the deformation in the bands is reversed. Only after the strain in all of the previously formed bands has been completely reversed, does deformation of the previously undeformed material begin. This additional deformation takes place by additional broadening of the shear bands. The stress required to broaden the bands in the reverse strain direction has the same magnitude as the stress which was required to cause the bands to broaden in the original strain direction. A typical reversed torque-twist curve for the polycarbonate samples is shown in Fig. 3. A shear band in the fully twisted and fully reversed state is shown in Fig. 4. If the direction of twisting is reversed again, the sequence of reversing the strain in the existing bands followed by additional band growth is repeated.

The density of the deformed material inside one of the bands was compared with the density of the undeformed material. It was found that the deformed material was approximately 0.1% more dense than the undeformed material. Annealing the samples at the glass transition temperature of the polymer, causes all of the strain to be recovered and the sample returns to its

original shape. When a deformed and annealed sample is retested, the entire deformation process is repeated. Bands form again at the same sites as before. This is believed to be because the bands are nucleated at stress concentrations introduced in machining the samples.

The results of these experiments indicate that the plastic deformation of a glassy polymer disrupts the structure of the material and produces a new structure in which the molecules can more readily slide over each other. The fact that the strain can be annealed out of the sample and that the original mechanical properties are recovered on annealing indicate that no significant amount of chain scission takes place during the deformation. The disruption of the original glassy structure of the polymer and the production of the weaker structure accounts for the strain softening and the fact that the material inside a shear band can be repeatedly deformed back and forth between plus and minus 70% shear strain at a stress less than that required to deform new material. The fact that the strain in the band saturates at ± 70% shear indicates that work-hardening occurs by molecular allignment. No work-hardening equivalent to that which occurs in metals and is a function of the integrated absolute value of the snear strain appears to occur.

B. Thermal Activation Parameters in Polyethylene and Polycarbonate

Deformation experiments were carried out on polycarbonate and polyethylene samples. The loading mode was torsion with a superimposed hydrostatic pressure. Experiments were carried out over a wide range of pressure, strain rate, and temperature. The results of the experiments were analyzed using the technique of thermal analysis to determine the activation parameters of the process. It was assumed that the deformation process is

described by the Arrhenius relationship

$$\dot{\varepsilon} = \dot{\varepsilon}_o \, exp \left(- \Delta \overset{*}{G} / kT \right) \tag{1}$$

and that the parameters of the process are defined in terms of the partial derivatives of ΔG^* as follows:

$$\text{Activation enthalpy} = H^* = \Delta G^* + T \Delta S^* = kT^2 \left(\frac{\partial \ln \dot{\varepsilon}/\dot{\varepsilon}_o}{\partial T} \right)_{T,P} \tag{2}$$

$$\text{Shear activation volume} = \Delta A^* = -\left(\frac{\partial \Delta G^*}{\partial T} \right)_{P,T} = kT \left(\frac{\partial \ln \dot{\varepsilon}/\dot{\varepsilon}_o}{\partial T} \right)_{P,T} \tag{3}$$

$$\text{Dilatation activation volume} = \Delta V^* = \left(\frac{\partial \Delta G^*}{\partial P} \right)_{T,T} = kT \left(\frac{\partial \ln \dot{\varepsilon}/\dot{\varepsilon}_o}{\partial P} \right)_{T,T} \tag{4}$$

where T is the absolute temperature, ΔS^* is the entropy change in the activation process, T is the shear stress, P is the hydrostatic pressure component of the stress, $\dot{\varepsilon}$ is the shear strain-rate, and ΔG^* is the energy required for activation.

The details of these experiments are reported in another publication (4),(The manuscript of this paper is submitted as Rept. No. DAHC04-71-C-0037-2). The important results are listed below:

1. Polycarbonate: Values of the activation parameters at room temperature, atmospheric pressure, and a strain-rate of $10^{-2}/\text{sec}$ are:

Activation enthalpy: 1.3×10^{-12} erg

Shear activation volume: $2.25 \times 10^{-21} \text{cm}^3$

Dilatation activation volume: $1.6 \times 10^{-22} \text{cm}^3$

2. Polyethylene: Values of the activation parameters at room temperature, atmospheric pressure, and a strain rate of $10^{-2}/\text{sec}$ are:

Activation enthalpy: 2.55×10^{-12} erg

Shear activation volume: 4.7×10^{-21} cm^3

Dilatation activation volume: 3.44×10^{-22} cm^3

Activation entropy (estimated): 8×10^{-15} erg/°K

It was concluded from these experiments that the shear yield stresses are a significant fraction of the shear modulus of the material, and the activation energies are quite large. This indicates that the mechanism of deformation is not the motion of some structural defect equivalent to the crystal dislocation, since there is no reasonable physical process which can acount for such a high resistance to the motion of such a defect. Furthermore, the large activation energies measured make the exponential term in the Arrhenius expression (Eq. (1)) very small of the order of 10^{-15} or smaller. A strain-rate of 10^{-2} can therefore be achieved only if the pre-exponential term is of the order of 10^{13} or greater. Such a large value of the pre-exponential practically requires that every monomer unit in the material be a potential site for thermal activation. This would again imply that deformation is not defect motion controlled. Existing structural defects can amount to only a small percentage of the total volume.

These observations would indicate that the mechanism of deformation is by the spontaneous nucleation of defects in the material. If the displacement associated with the defect is pure shear, such a defect would be analogous to a dislocation loop as proposed by Bowden and Raha (5). If an angular change is also involved in the defect created, the defect could be analogous to a disclination pair as proposed by Argon (6).

C. A Metallic Replica Technique for Scanning Electron Microscopy

In the experiments to examine the microstructural aspects of deformation, one serious problem was obtaining a picture of the structure with sufficiently high resolution to evaluate the structural changes which were taking place. In this work, attempts were made to use shadowed carbon and plastic replicas viewed either in the transmission or scanning electron microscope, and direct observation of the metallized polymer in the scanning microscope. With carbon replicas in the transmission microscope, only a small portion of the surface could be viewed at one time and it was difficult to relate the orientation and position of the portion which was examined to the deformed sample. Plastic replicas and the metallized sample itself were found to be unsuitable for high magnification examination because the heating of the electron beam caused them to deform. This thermally induced deformation obscured much of the detail which was to be observed.

A technique was developed for making a thick metallic replica by a combination of vapor deposition and electroplating. (7). (The manuscript of this paper is submitted as Rept. No. DAHC04-71-C-0037-3.) This replica technique involves vapor depositing a 1000 $\overset{\circ}{A}$ thick layer of gold paladium alloy on the surface to be replicated and then plating this layer with nickel to a thickness of 0.1 mm. This metal replica is then stripped from the polymer surface. This replicating technique has several advantages over other methods:

1. The surface viewed is an exact mirror image of the surface to be studied having been   in direct contact with the other surface when it was formed. Thus no detail is obscured as can be the case when a non-

metallic surface is metallized by depositing a 200 - 300 Å thick metal layer over it for direct viewing in the scanning microscope.

2. The replica is mechanically strong enough so that it cannot be deformed when it is stripped from the surface of the sample.

3. The replica is electrically and thermally conductive so that no electrical charging occurs and the local heating by the electron beam is kept small enough to avoid any distortion of the replica.

D. **Microstructural Examination of the Mechanisms of Plastic Deformation in Extended Chain Polyethylene**

These experiments were performed on extended chain polyethylene (Marlex 6009). Samples were prepared by crystallizing the molten polymer, which was sealed in a thin walled silver tube at $230°C$ under a hydrostatic pressure of 5 kbar. The material was maintained at temperature and pressure for seven hours during crystallization, and then cooled at a rate of $2°C/min$ while the pressure was maintained. The material produced was a spherulitic extended chain structure with lamellae with thicknesses between 0.5 and 1.0μ. The specific gravity of the material was in the range 0.98 - 0.99.

Compression samples were machined from the material and they were mechanically polished. The damage produced by the machining and polishing was removed by ion etching the samples at $77°K$ using a 3.5 kV argon ion beam of intensity $15\,\mu Amp/cm^2$. The ion etching left an amorphous skin on the surface of the material, but it was found that this skin could be peeled off by applying replica tapes to the surface and then stripping

then off. When the replica tapes were removed, the amorphous skin adhered to the replica tape and was removed from the surface. This process produced a surface in which all of the fine details of the spherulitic structure were clearly visible when it was examined using the replica technique described above.

One of the results of this surface preparation technique was to reveal that the spherulitic structure in this material is not made up of twisted ribbon like lamellae. The lamellae in the extended chain material appear to be leaf like, being wrapped around the spherulite like the leaves of an artichoke. This structure is described in more detail elsewhere (7).

The samples of the extended chain material were deformed in compression to strains up to 30%. The yield stress of the material was found to be 5 kg/mm^2 which is greater than the yield stress of ordinary polyethylene. Some samples fractured without yielding.

Low magnification microscopic examination of the material revealed that the deformation took place on discrete shear bands which formed very close to the maximum shear stress directions at $\pm 45°$ from the tensile axis. The strain inside the bands was estimated to be 50%. The width of the bands was approximately $3 - 5\mu$ and their length was $50 - 100\mu$. This compares with the spherulite diameter of approximately 20μ. The shear bands had no fixed relationship to the spherulite structure, and crossed the spherulites at essentially random locations relative to the spherulite center. At the magnification which can be achieved in the optical microscope, the shear bands appeared to be relatively unaffected by the microstructure of the polymer indicating that the spherulitic structure is quite flexible and contains a multiplicity of the deformation modes sufficient to accomodate

nearly any imposed deformation.

High resolution microscopy in the scanning electron microscope of replicas of the samples prepared in the manner described in Sec. II.C reveal that on a scale of lamella dimensions, the deformation in the shear bands is not as uniform as it appears in the lower magnification studies. This appears to be the result of the fact that the direction through the lamella thickness parallel to the molecular direction is inextensible. The deformation, therefore, compensates for this restriction by concentrating in other regions and by shearing of the lamella in directions parallel to the molecules and rotation of the lamella. The multiplicity of the deformation modes appears to be sufficient that when the strains are averaged over several lamella thicknesses, any imposed strain can be produced. This is consistent with the low magnification observation that the average strain in a band of $2 - 5\,\mu$ thickness is independent of the structure.

Detailed observations reveal the existence of a number of deformation modes. Evidence of many of these modes is visible in Fig. 5.

1. Slip on planes parallel to the molecule with the slip direction perpendicular to the molecule. Fig. 6 (a).

2. Intralamellar slip on planes parallel to the molecule with the slip direction parallel to the molecule. Fig. 6 (b).

3. Formation of kinks in the lamellae. Fig. 6 (c).

4. Interlamellar shear.

The first two modes are sufficient to allow slip on any plane which contains the molecule direction, and in any direction on such a plane. Shear in the direction perpendicular to the molecule is accomplished by shear parallel

to the molecule accompanied by rotation of the lamella. Fig. 6 (d). Such
a mode allows the lamella to get thinner and longer. Shortening of the
thickness of the lamella can also be accomplished by the formation of kinks
as shown in Fig. 6 (c). The only deformation which appears to be impossible
is an extension of the lamella thickness.

III. Conclusions about the Nature of Plastic Deformation in Polymer Structures.

Plastic deformation of amorphous polymer structures occurs only at
shear stresses close to the theoretical strength of the material. The process
is thermally activated and there are strong indications that the microscopic
process is one of nucleation of dislocation or disclination like loops in
previously "defect free" material. Because the stresses required are as high
relative to the modulus of the material as they are, and because deformation
does not appear to require pre-existing defects, there appears to be little
promise of improving the shear strength of polymers by structural control
as is practiced in metals. Improvements in the shear strength of polymers
will have to come from changes in the nature of the chemical bonding within
the polymer as in ionomers and covalently cross-linked structures.

In crystalline polymers, deformation appears to occur by a combination
of interlamellar shear in the lamellae boundaries, and intralamellar shear
which can occur on any plane parallel to the molecule direction. The mech-
anism by which this deformation is produced is undetermined, and it is not
known what part of the deformation process controls the overall strain-rate.
Motion of dislocations through the crystalline lamellae cannot be ruled out

as a deformation mechanism. The complex spherulitic structure is highly
inhomogeneous and anisotropic, and it would appear that it would be difficult
to find compatible shear paths through the structure. Experimentally this
is not found to be the case. The multiplicity of the shear modes in the
structure is sufficient to accomodate any imposed shear deformation if the
strain can be averaged over several lamella thicknesses.

IV. Publications

1. "Shear Bands in Polycarbonate," W. Wu and A. P. L. Turner.
   Submitted to Journal of Polymer Science.

2. "Thermal Activation Parameters for Large Strain Deformation of
   Polyethylene and Polycarbonate," W. Wu and A. P. L. Turner.
   Submitted to Journal of Polymer Science.

3. "A Metallic Replica Technique for Scanning Electron Microscopy,"
   W. Wu, A. S. Argon and A. P. L. Turner. Submitted to Journal
   of Materials Science.

4. " Molecular Mechanisms of Plastic Deformation in Extended Chain
   Polyethylene," W. Wu, A. P. L. Turner. Manuscript in preparation.

V. Personnel Associated with this Work and Advanced Degree Received

1. A. P. L. Turner - Assistant Professor of Mechanical Engineering
                     Principal Investigator

2. W. Wu - Graduate Student Research Assistant, July 1971 - May 1972
           Post Doctoral Research Fellow, June 1972 - June 1973.
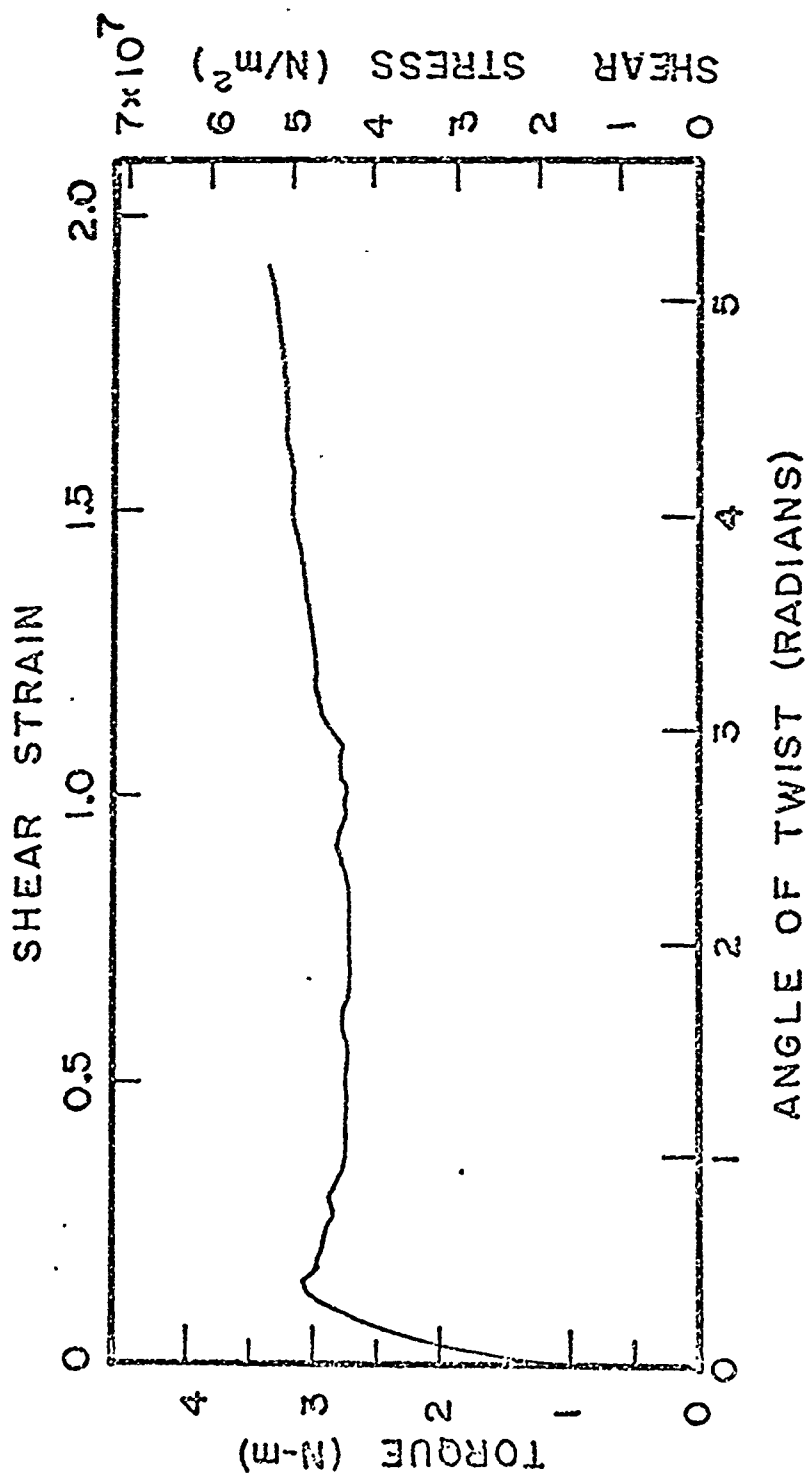   Ph. D. received June, 1972.

VI. References

1. A. S. Argon, R. D. Andrews, J. A. Godrick and W. Whitney, J. Appl. Phys. 39, 1899, (1968).

2. J. C. Bauxens, J. Polymer Sci. A2 8, 893 (1970).

3. W. Wu. and A. P. L. Turner, "Shear Bands in Polycarbonate," to be published in J. Polymer Sci. Manuscript submitted to U. S. Army Research Office - Durham as project Rept. No. DAHC04-71-C-0037-1.

4. W. Wu and A. P. L. Turner, "Thermal Activation Parameters for Large Strain Deformation of Polyethylene and Polycarbonate," submitted to J. Polymer Sci. Manuscript submitted to U. S. Army Research Office - Durham as project Rept. No. DAHC04-71-C-0037-2.

5. P. B. Bowden and S. Raha, "A Molecular Model for Yield and Flow in Amorphous Glassy Polymers Making Use of a Dislocation Analogue," to be published in Phil. Mag.

6. A. S. Argon, "A theory for the Low Temperature Plastic Deformation of Glassy Polymers," to be published in Phil. Mag.

7. W. Wu, A. S, Argon, and A. P. L. Turner, "A Metallic Replica Technique for Scanning Electron Microscopy," to be published in J. Mater. Sci. Manuscript submitted to U. S. Army Research Office - Durham as project Rept. No. DAHC04-71-C-0037-3.
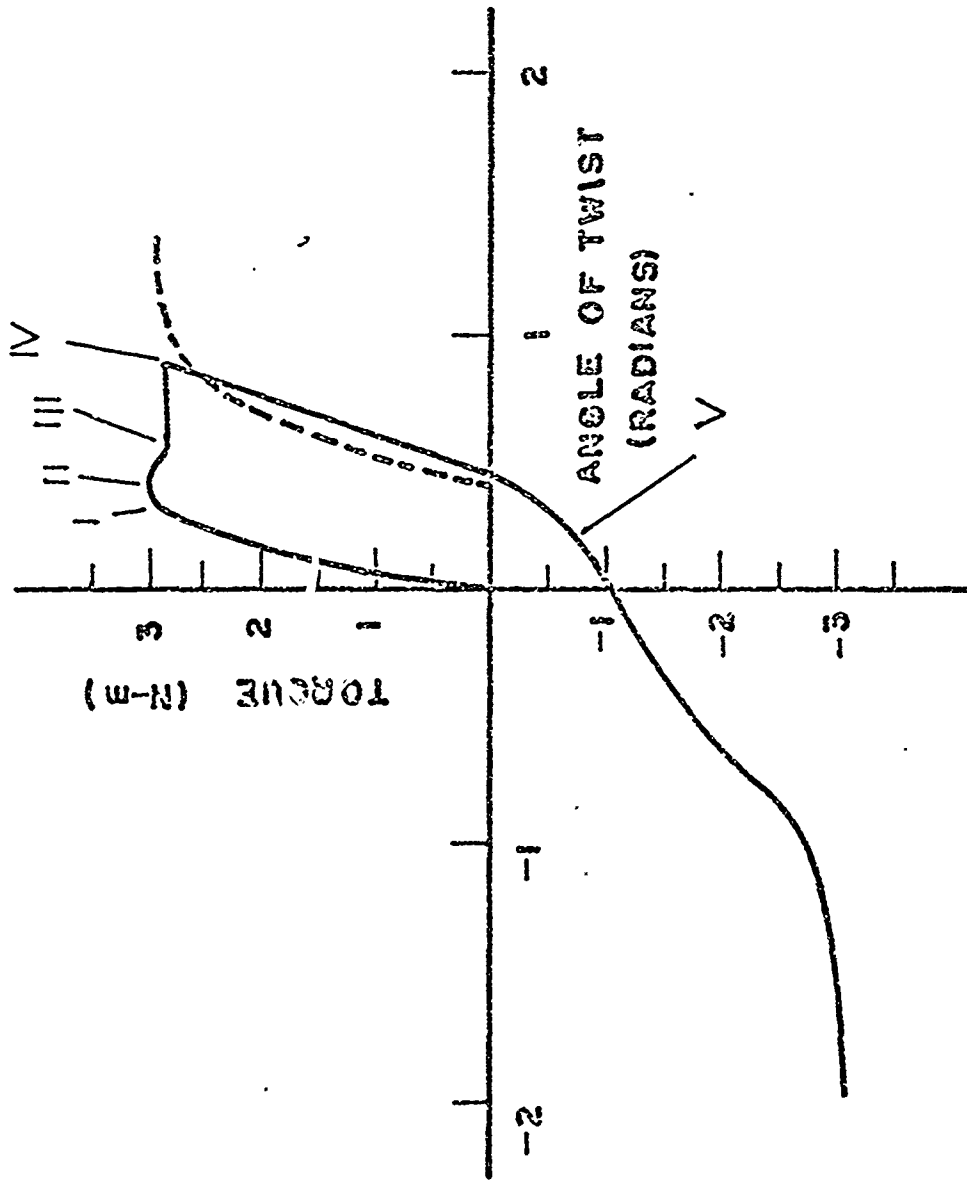
VII. Figures

1. Torque-twist curve for the deformation of polycarbonate torsion samples.

2. Various stages of deformation band development. (a) Fine bands formed at yield. (b) Broadening of bands. (c) Further development of the bands. (d) Uniform reversal of the shear in the bands during untwisting.

3. Typical reverse torque-twist curve for polycarbonate torsion sample. Dashed line indicates reloading path for sample which has been unloaded and allowed to relax.

4. Shear band sheared in the forward direction (a). Untwisted to zero residual strain (b). Twisted to the fully reversed strain (c).

5. Structure of a deformed spherulite in extended chain polyethylene.

6. Modes of deformation in a lamellar structure. (a) Shear perpendicular to the molecule direction. (b) Shear parallel to the molecule direction. (c) Kink formation to shorten the lamella thickness. (d) Shear on a plane perpendicular to the molecule is accomplished by shear parallel to the molecule and rotation of the lamella.

Fig 3

SHEAR STRESS (N/m²)

7×10⁷

SHEAR STRAIN

ANGLE OF TWIST (RADIANS)

TORQUE (N-m)

TORQUE (N-m)

ANGLE OF TWIST (RADIANS)

I II III IV V

2 (a)

2 (b)

2 (c)

2 (d)

FIG. 4a

FIG. 4b

FIG. 4c

FIG. 4d

4 (a)

4 (b)

4 (c)

FIG. 5a

FIG. 5b

FIG. 5c

2